

Kinetics and mechanism of thermal decomposition of nickel, manganese, silver, mercury and lead oxalates

Boris V. L'vov*

Department of Analytical Chemistry, St. Petersburg State Technical University, St. Petersburg 195251, Russia

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Abstract

A model of dissociative evaporation of the reactant with simultaneous condensation of the low-volatility product has been invoked to interpret the reaction schemes of the thermal decompositions of nickel, manganese, silver, mercury and lead oxalates. A critical analysis of literature data and their comparison with theoretical calculations permitted selection of two different schemes: with the evolution of $\text{CO} + \text{CO}_2 + \frac{1}{2}\text{O}_2$ (or O) as primary products for Ag, Ni and Hg oxalates, and evolution of $2\text{CO} + \frac{1}{2}\text{O}_2$, for Mn and Pb oxalates. The validity of the proposed decomposition schemes is supported by good agreement of experimental values of activation energies E_a and initial decomposition temperatures T_{in} with their theoretical values. As an additional criterion for correct selection of the primary-product composition, the depressing effect exerted on the decomposition rate by one of the assumed gaseous products was used. Some of the features of the oxalate decomposition were interpreted. Among them are the low values of decomposition coefficients; a correlation between T_{in} and E_a parameters; a difference between activation energies for induction and acceleratory periods in the decomposition of NiC_2O_4 and $\text{Ag}_2\text{C}_2\text{O}_4$ and the existence of long induction periods in the process of decomposition of all the oxalates except for HgC_2O_4 . © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Thermal decomposition of metal oxalates has been the subject of many investigations for more than a century. It will suffice to mention, that the first work on PbC_2O_4 decomposition was published in 1870 [1]. There are several reviews devoted to this problem, e.g. [2–5]. The most comprehensive discussion of this subject is contained in a book by Galwey and Brown [6] published recently. The decomposition of some of the oxalates ($\text{Ag}_2\text{C}_2\text{O}_4$ and NiC_2O_4) serves as a model

for theoretical speculations. Nevertheless, many features of oxalate decomposition still remain unclear. As an example, two important points can be mentioned. First, one cannot find an explanation for the tremendous difference between the equilibrium partial pressure of CO_2 at the initial temperature of $\text{Ag}_2\text{C}_2\text{O}_4$ decomposition (about 90°C) reaching 10^{17} atm, on one hand, and the equivalent partial pressure of CO_2 (about 10^{-6} atm) corresponding to the decomposition rate of $\text{Ag}_2\text{C}_2\text{O}_4$ at this temperature, on the other. Second, no quantitative interpretation of the difference between activation energies for the induction and acceleratory periods (216 and 159 kJ mol^{-1} [7], respectively) for NiC_2O_4 decomposition in vacuum has been put forward until now.

* Tel.: +7-812-552-7741; fax: +7-812-247-4384.

E-mail address: blvov@robotek.ru (B.V. L'vov).

The objective of this work is to discuss the mechanism and some features of oxalate decomposition using a model of *dissociative evaporation of the reactant with simultaneous condensation of the low-volatility product*. This approach has been employed earlier to explain the mechanism and kinetics of thermal decomposition of nitrates [8–10], azides [11], carbonates [12], $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [13], $\text{Mg}(\text{OH})_2$ [14], Ag_2O [15], HgO [16], GaN [17] and of a number of other inorganic compounds [18–21]. The choice of objects for the present investigation has been defined by the availability of reliable thermodynamic functions for metal oxalates.

2. Theoretical

2.1. Concepts

Our approach [8–21] to interpretation of decomposition mechanisms differs radically from the one accepted universally. Classical TA attempts to understand the differences between the experimentally measured and theoretically predicted kinetic parameters of the decomposition process assuming the primary decomposition products have an equilibrium composition. To account for the discrepancies between calculation and experiment (most frequently, in the magnitude of E_a), one invokes either physical

reasons (e.g. depressed diffusion of a gaseous product from the solid matrix) or some chemical stages associated with the transport of electrons, protons, positive holes, or ions among groups of atoms or ions. These explanations usually do not contain any quantitative estimates.

Our approach is based on the assumption that the decomposition process itself reduces to congruent dissociative evaporation of the reactant, so that the kinetics of the process is determined only by the composition of the primary decomposition products and the experimental conditions, which govern the evaporation mode and reactant self-cooling. Thus, the search for an adequate decomposition mechanism reduces primarily to look for a composition of primary evaporation products for which the calculated kinetic parameters would be in agreement with experiment. Fig. 1 illustrates the principal differences between the universally accepted (standard) and proposed approaches.

2.2. Calculation scheme

The calculations are based on the classical evaporation model of Hertz–Langmuir, applied to the cases of dissociative evaporation of compounds. The scheme of theoretical calculation of the main kinetic parameters (the flux of the gaseous product J , the rate constant k , the product partial pressure P and the

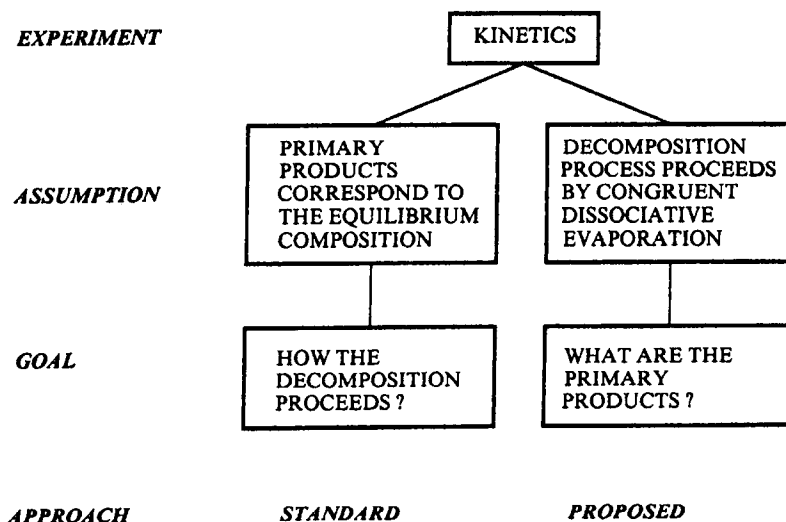
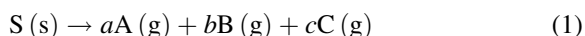


Fig. 1. Simplified schemes of standard and proposed approaches to the investigation of decomposition mechanisms.

parameters of the Arrhenius equation, E_a and A) has been described in a number of previous publications [11–21]. Therefore, we are going to present below only some final relations necessary for the calculations in this work.

In the case of a compound S decomposed in vacuum into gaseous products A, B and C



the flux of product A can be expressed through the equivalent partial pressure P_A (atm) of this product corresponding to the hypothetical equilibrium of reaction (1) in the form

$$J_A = \frac{\gamma M P_A}{(2\pi M_A R T)^{1/2}} \quad (2)$$

where M and M_A are the molar masses of the reactant and product A, γ the coefficient of conversion from atmospheres to pascals, and R the gas constant.

The theoretical value of the partial pressure of product A can be calculated from the equilibrium constant K_P for reaction (1). In the absence of reaction products in the reactor atmosphere, the situation corresponding to the *equimolar* evaporation mode, the partial pressure P_A can be expressed as [19]

$$\begin{aligned} P_A^e &= a \left(\frac{K_P}{F}\right)^{1/v} \left(\frac{M_A}{M_B}\right)^{b/2v} \left(\frac{M_A}{M_C}\right)^{c/2v} \\ &= \frac{a}{F^{1/v}} \left(\frac{M_A}{M_B}\right)^{b/2v} \left(\frac{M_A}{M_C}\right)^{c/2v} \exp\left(\frac{\Delta_r S_T^\circ}{vR}\right) \\ &\quad \times \exp\left(-\frac{\Delta_r H_T^\circ}{vRT}\right) \end{aligned} \quad (3)$$

Here $\Delta_r H_T^\circ$ and $\Delta_r S_T^\circ$ are the changes of the enthalpy and entropy, respectively, in process (1).

If the partial pressure P'_B of one of the gaseous components (B) greatly exceeds the equivalent pressure P_B of the same component released in the decomposition and if, in addition to that, the magnitude of P'_B remains constant in the process of decomposition, we call such an evaporation mode *isobaric*. In this case

$$\begin{aligned} P_A^i &= \frac{K_P^{1/(a+c)}}{P'_B b/(a+c)} \left(\frac{M_A}{M_C}\right)^{c/2(a+c)} \\ &= \frac{1}{P'_B b/(a+c)} \left(\frac{M_A}{M_C}\right)^{c/2(a+c)} \exp\left(\frac{\Delta_r S_T^\circ}{(a+c)R}\right) \\ &\quad \times \exp\left(-\frac{\Delta_r H_T^\circ}{(a+c)RT}\right) \end{aligned} \quad (7)$$

As can be seen from Eqs. (3) and (7), the calculated activation energies for reaction (1) should be different for the equimolar and isobaric modes of decomposition, i.e.

$$E_a^e = \frac{\Delta_r H_T^\circ}{a+b+c} \quad (8)$$

for the equimolar mode and

$$E_a^i = \frac{\Delta_r H_T^\circ}{a+c} \quad (9)$$

for the isobaric one.

Taking logarithms and solving Eq. (3) for the temperature contained in the enthalpy factor, we obtain the following relation for the calculation of the initial decomposition temperature:

$$T_{in} = \frac{\Delta_r H_T^\circ}{\Delta S_T^\circ + vR[\ln v - \ln(F/v) + (b/2v)\ln(M_A/M_B) + (c/2v)\ln(M_A/M_C) - \ln P_\Sigma]} \quad (10)$$

where

$$F \equiv a^a \times b^b \times c^c \quad (4)$$

$$v = a + b + c \quad (5)$$

and

$$K_P = P_A^a P_B^b P_C^c \quad (6)$$

where $P_\Sigma \equiv (v/a)P_A$.

In order to take into account the partial transfer of the energy released in the condensation of low-volatility product A to the reactant, we introduced, as before [15–17,21], into calculations of the enthalpy of decomposition reaction (1) an additional term $\tau a \Delta_c H_T^\circ(A)$, where the coefficient τ corresponds to the fraction of the condensation energy transferred to

the reactant. Thus, we can write

$$\Delta_f H_T^\circ = a\Delta_f H_T^\circ(\text{A}) + b\Delta_f H_T^\circ(\text{B}) + c\Delta_f H_T^\circ(\text{C}) - \Delta_f H_T^\circ(\text{S}) + \tau a\Delta_c H_T^\circ(\text{A}) \quad (11)$$

The most plausible of all conceivable mechanisms of the energy transfer appears to be thermal accommodation [22,23] or, in other words, direct transfer of the energy at the reaction interface in collisions of the low-volatility molecules with the reactant and product surface. For equal temperatures of the solid phases, one may expect equipartition of energy between the two phases, i.e. $\tau = 0.5$. It should be mentioned that the choice of the τ magnitude, as well as the mechanism responsible for the condensation energy transfer to the reactant are the most weak points of the theory as a whole. For majority of substances investigated up to now, the condition $\tau = 0.5$ is valid. Exceptions from this rule are only some solid compounds which are decomposed with the formation of H_2O as one of the primary products, e.g. $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ [13] and $\text{Mg}(\text{OH})_2$ [14]. For these substances: $\tau \cong 0.6$. We have no explanation for this difference.

2.3. Thermodynamic functions

In available handbooks [24–26], we could find more-or-less reliable thermodynamic data ($\Delta_f H_{298}^\circ$ and S_{298}°) only for the oxalates of Ni, Ag and Pb (Table 1). For the oxalates of Mn and Hg, there are only the values of enthalpies of formation ($\Delta_f H_{298}^\circ$) but no entropy functions. To estimate these values, we compared the entropy values of some other Mn and Hg compounds with the entropy values of the same compounds of Ni and Pb (Tables 2 and 3, respectively). As can be seen from Table 2, for all oxycompounds of manganese, S_{298}° functions are systematically higher than that for nickel. The average difference equals $9.2 \text{ J mol}^{-1} \text{ K}^{-1}$. Therefore, the entropy value for MnC_2O_4 was taken to be $9.2 \text{ J mol}^{-1} \text{ K}^{-1}$ higher than that for NiC_2O_4 . For Hg and Pb compounds (Table 3), the entropy values are practically the same. Therefore, the entropy value for HgC_2O_4 was taken to be equal to that for PbC_2O_4 . For MnC_2O_4 , we took into account, in addition to the enthalpy value ($-1029.7 \text{ kJ mol}^{-1}$) from [24], the more recent determinations of enthalpy (-1008.3

Table 1
Thermodynamic functions [24–26] used in the calculations

Species	State of aggregation	ΔH_{298}° (kJ mol ⁻¹)	S_{298}° (J mol ⁻¹ K ⁻¹)
Ni	s	0	29.9
Ni	g	428.8	182.1
NiC ₂ O ₄	s	-863.2	132.9
MnO	s	-385.1	61.5
MnO	g	123.8	226.4
MnC ₂ O ₄	s	-1016.7 ^a	142.1 ^b
Ag	s	0	42.6
Ag	g	284.9	172.9
Ag ₂ C ₂ O ₄	s	-674.5	181.1
Hg	l	0	75.9
Hg	g	61.4	174.9
HgC ₂ O ₄	s	-672.8	146.0 ^c
PbO	s	-218.6	67.8
PbO	g	68.1	239.9
PbC ₂ O ₄	s	-851.0	146.0
CO	g	-110.5	197.5
CO ₂	g	-393.5	213.7
O	g	249.2	160.9
O ₂	g	0	205.0

^a The averaged value from: $-1029.7 \text{ kJ mol}^{-1}$ [24]; $-1008.3 \text{ kJ mol}^{-1}$ [27]; $-1012.0 \text{ kJ mol}^{-1}$ [28].

^b Our estimation based on the comparison of entropy values (Table 2).

^c Our estimation based on the comparison of entropy values (Table 3).

Table 2
The entropy of some solid oxyc compounds of Mn and Ni [24,25]

Compound	S_{298}° (J mol ⁻¹ K ⁻¹)		
	Manganese	Nickel	Difference
MO	59.8 ± 2.0	38.1 ± 0.4	21.7
M(OH) ₂	94.9 ± 8.0	80.0 ± 0.6	14.9
MSO ₄	112.5 ± 1.2	103.8 ± 1.0	8.7
MCO ₃	85.8 ± 1.2	85.3 ± 1.2	0.5
MAI ₂ O ₄	103.8 ± 2.0	98.3 ± 4.0	5.5
MCr ₂ O ₄	133.9 ± 2.0	124.3 ± 8.0	9.6

Table 3
The entropy of some solid compounds of Hg and Pb [24]

Compound	S_{298}° (J mol ⁻¹ K ⁻¹)		
	Mercury	Lead	Difference
MO	70.3 ± 0.2	68.8 ± 1.2	1.5
MS	82.4 ± 0.4	91.2 ± 1.2	-8.8
MSe	99.0 ± 0.8	102.5 ± 2.0	-3.5
MTe	111.5 ± 0.6	110.0 ± 2.0	1.5
MCl ₂	140.0	134.3 ± 2.0	5.7
MSO ₄	153.7	148.6 ± 0.6	5.1

and -1012.0 kJ mol⁻¹) in [27,28]. As can be seen from the above, the error of estimation of enthalpy and entropy values for some oxalates may run to 10 kJ mol⁻¹ and 10 J mol⁻¹ K⁻¹, respectively.

3. Results and discussion

3.1. Autocatalysis

As was discussed in our previous works [15,20], the model of congruent dissociative evaporation of reactant with simultaneous condensation of the low-volatility product at the reactant/product interface provides a straightforward explanation for a number of features in the solid-state decomposition process which have not yet found convincing interpretation, in particular, the mechanism of primary single-step nucleation and the origin of energy supported the autocatalytic development of many decomposition reactions. In the framework of our approach, the mechanism of nucleation through condensation of supersaturated vapour of the low-volatility product is fairly obvious [22]. The transfer of one-half of the condensation energy to the reactant in the process of collisions of the low-vola-

tility molecules with the reactant and product surface at the interface zone explains the increase in decomposition rate.

In the case of the oxalates under investigation, the appearance of an induction period and the sigmoid shape of the yield-time curves should be expected only for those compounds which decompose with the formation of low-volatility products (metals or oxides). This is valid for the oxalates of Ni, Ag, Mn and Pb but not for mercury oxalate. A careful analysis of the literature supports this conclusion. Indeed, the induction period observed in vacuum for the first four oxalates ranges up to about 200 min for NiC₂O₄ at 230°C [7], 120 min for Ag₂C₂O₄ at 110°C [29], 40 min for PbC₂O₄ at 309°C [30] and 20 min for MnC₂O₄ at 243°C [31]. For HgC₂O₄, the induction period is absent at 180°C (see Fig. 2 in [32]) or does not exceed 5 min at 190°C [32]. A slight increase of the decomposition rate in the last case can be explained by thermal equilibration after introduction of a Pt bucket with the sample into the furnace.

3.2. Activation energies and initial temperatures

The main criterion for the selection of appropriate schemes of decomposition of the oxalates under study was the agreement between experimental and theoretically calculated values of activation energies (E_a) and initial temperatures (T_{in}). Table 4 contains the values (arranged in decreasing order) of both parameters taken from 25 different works [2,7,29–38,40–49,51,52] published in the period between 1935 and 1974, and two works [39,50] published in the 1990s. Most of these data were measured in vacuum. Initial decomposition temperatures, measured in nitrogen or inert gases, are marked in italics. When, in the same work, several values of the activation energy were obtained by different methods, we used the average value. For example, Macdonald [42] has found three values of activation energy for decomposition of Ag₂C₂O₄: 137, 149 and 161 kJ mol⁻¹. So, the average value $E_a = 149 \pm 12$ kJ mol⁻¹.

In selection of appropriate schemes of decomposition for different oxalates, we varied the composition of primary gaseous products (CO, CO₂ and O/O₂) to satisfy the best agreement between calculated and experimental parameters. Of the two parameters (E_a and T_{in}), preference was given to the initial tempera-

Table 4
Activation energies and initial temperatures for the thermal decomposition of the oxalates under study

Implied reaction	ν	F	τ	E_a (kJ mol ⁻¹)		T_{in} (K)	
				Calculated	Experimental	Calculated ^a	Experimental ^b
NiC ₂ O ₄ → Ni (g) + CO + CO ₂ + $\frac{1}{2}$ O ₂	3.5	0.707	0	225	216 [7]	568	<i>612</i> [2], <i>591</i> [36], <i>571</i> [39], <i>563</i> [38], <i>542</i> [33], <i>535</i> [37], <i>526</i> [35], <i>513</i> [34], <i>503</i> [7]
				0.5	164		
MnC ₂ O ₄ → MnO (g) + 2CO + $\frac{1}{2}$ O ₂	3.5	2.828	0.5	190	180 [40], 171 [2], 141 [41]	651	<i>673</i> [41], <i>655</i> [2], <i>616</i> [36], <i>610</i> [31], <i>608</i> [40]
Ag ₂ C ₂ O ₄ → 2Ag (g) + CO + CO ₂ + $\frac{1}{2}$ O ₂	4.5	2.828	0	165	172 [49], 149 [42]	363	<i>413</i> [48], <i>410</i> [45], <i>408</i> [46], <i>399</i> [47], <i>385</i> [49], <i>378</i> [44], <i>373</i> [29,42], <i>360</i> [43]
				0.5	101		
HgC ₂ O ₄ → Hg (g) + CO + CO ₂ + O	4.0	1	0	120	110 [51], 107 [32]	424	<i>453</i> [32], <i>373</i> [51]
PbC ₂ O ₄ → PbO (g) + 2CO + $\frac{1}{2}$ O ₂	3.5	2.828	0.5	159	151 [30]	532	<i>582</i> [30], <i>577</i> [36], <i>>523</i> [52]

^a At total equivalent pressure, $P_T = 10^{-6}$ atm.

^b Decomposition temperatures measured in nitrogen or inert gases at 1 atm are marked in italics.

tures (as statistically more reliable). In the interpretation of experimental values of activation energies for NiC_2O_4 and $\text{Ag}_2\text{C}_2\text{O}_4$ we took into account the existence of two extreme modes of decomposition: an initial stage in the absence of a reaction interface ($\tau = 0$) and a steady-state mode in the presence of a reaction interface ($\tau = 0.5$).

The reaction schemes chosen as a result of this selection and the corresponding values of activation energies and initial temperatures are presented in Table 4. For the calculation of activation energies, Eqs. (8) and (11) were used. For the calculation of initial temperatures, Eq. (10) was used. The total pressure of the products (P_Σ) corresponding to the initial decomposition of oxalates was taken to be 10^{-6} atm. This value is in accord with our previous estimations [21] based on the use of two practically important parameters: the average initial radius of reactant particles and the total time of their decomposition. As can be seen from Table 4, there are two different schemes of oxalate decomposition: with the evolution of $\text{CO} + \text{CO}_2 + \frac{1}{2}\text{O}_2$ (or O) as primary products for Ag, Ni and Hg oxalates, and evolution of $2\text{CO} + \frac{1}{2}\text{O}_2$, for Mn and Pb oxalates. The composition of these gaseous products in both cases differs from the equilibrium compositions (2CO_2 and $\text{CO} + \text{CO}_2$, respectively).

The results of theoretical calculations are in very satisfactory agreement with experimental data. This can be seen from the correlation of experimental and theoretical values of initial temperatures presented graphically in Fig. 2. The relative standard deviation of experimental points ($n = 28$) from the line corresponding to the ideal correlation is only 6.5% or about 30 K. There are only two points (for NiC_2O_4) which deviate from the line by more than 50 K. However, both these points correspond to the temperatures of the nucleation stage [7,34]. We consider this agreement as strong proof of the validity of the decomposition schemes presented in Table 4.

The calculated values of the activation energies are also in agreement with experimental values, though the scatter of experimental data is larger, partly due to some arbitrariness in the selection of the appropriate kinetic models by different authors. Nevertheless, as a whole, the agreement is quite satisfactory. Of fundamental importance is the observation for NiC_2O_4 and $\text{Ag}_2\text{C}_2\text{O}_4$ of the difference in the activation energies for the nucleation and steady-state stages of decomposition. In the framework of our model, this difference, ΔE_a obeys the relationship

$$\Delta E_a = \frac{\tau a \Delta_c H_T^\circ (A)}{v} \quad (12)$$

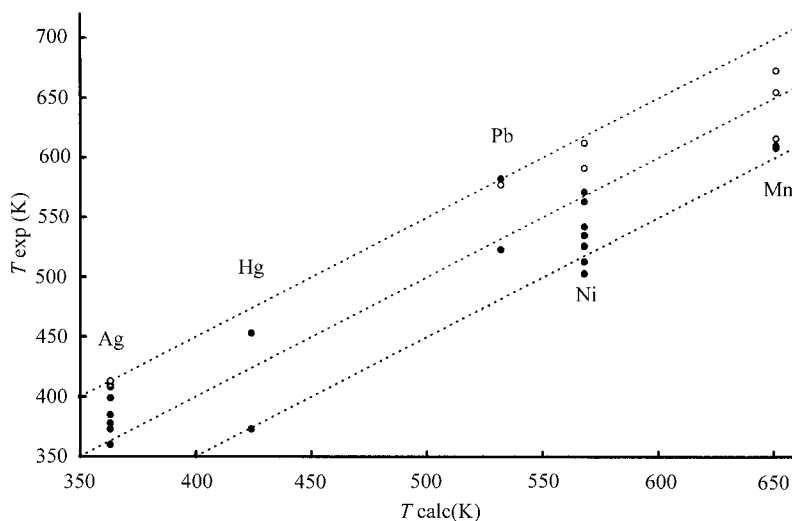


Fig. 2. Correlation between experimental and calculated values of initial decomposition temperatures for different oxalates. Central dotted line corresponds to the ideal correlation. Two other lines are shifted in a vertical direction by ± 50 K. Experimental points are taken from Table 4. Symbols: (●) vacuum; (○) N_2 atmosphere.

Table 5

Calculated activation energies and initial temperatures for the thermal decomposition of Mn and Pb oxalates in line with the generally accepted ratio $\text{CO}/\text{CO}_2 = 1$

Implied reaction	ν	F	τ	E_a (kJ mol ⁻¹)	T_{in}^a (K)
$\text{MnC}_2\text{O}_4 \rightarrow \text{MnO}(\text{g}) + \text{CO} + \text{CO}_2$	3.0	1.0	0.5	127	442
$\text{PbC}_2\text{O}_4 \rightarrow \text{PbO}(\text{g}) + \text{CO} + \text{CO}_2$	3.0	1.0	0.5	91	304

^a At total equivalent pressure, $P_{\Sigma} = 10^{-6}$ atm.

where, as before, $\tau a \Delta_c H_T^\circ$ (A) is the part of the condensation energy transferred to the reactant by the low-volatility product A. For both oxalates, the calculated and experimental values of ΔE_a are about 60 kJ mol⁻¹. It proves the validity of the condition: $\tau = 0.5$ (see Section 2.2).

We are aware that the compositions of the gaseous products in the suggested schemes are in contradiction with the results of many GC and MS experimental measurements. There is a simple explanation of this fact. Unfortunately, all these measurements have been performed under conditions when the secondary equilibration of the composition was not excluded. It is remarkable that even under these conditions, the ratio CO/CO_2 in some experiments (e.g. [31]) was higher than the equilibrium one. The only way to detect the primary products of decomposition in their original proportion consists in the elimination of any collisions of these species with the furnace and the quadruple spectrometer walls on their way from sample to ionizer, as has been done in [9,10].

To illustrate the effect of composition of gaseous products on kinetic parameters, we calculated (Table 5) the activation energies and initial temperatures for the thermal decomposition of Mn and Pb oxalates in line with the generally accepted ratio $\text{CO}/\text{CO}_2 = 1$. It can be seen that both parameters

in this case are far less (by ca. 60 kJ mol⁻¹ for E_a and 200 K for T_{in}) than those listed in Table 4.

At this point, an important correlation between T_{in} and E_a parameters should be mentioned. As can be seen from Table 6, for all the oxalates decomposed in vacuum under steady-state conditions, the ratio T_{in}/E_a is practically constant and equals 3.5 ± 0.1 for the calculated and 3.6 ± 0.2 for experimental (averaged) data. This regularity was noted earlier in relation to the decomposition of oxides [19]. In that case, $T_{\text{in}}/E_a \cong 3.8$. The origin of this correlation between T_{in} and E_a parameters is rather obvious. If we neglect the stoichiometric items in the denominator in Eq. (10) and take into account Eq. (8), we obtain

$$\begin{aligned} \frac{T_{\text{in}}}{E_a} &\cong \frac{\nu}{\Delta S_T^\circ + \nu R(\ln \nu - \ln P_{\Sigma})} \\ &= \frac{1}{\Delta S_T^\circ/\nu + R(\ln \nu - \ln P_{\Sigma})} \end{aligned} \quad (13)$$

Taking into account that for oxalates under study $\Delta S_{298}^\circ/\nu \cong 159 \pm 10 \text{ J mol}^{-1} \text{ K}^{-1}$, $\nu \cong 4 \pm 0.5$ and $P_{\Sigma} = 10^{-6}$ atm, we obtain $T_{\text{in}}/E_a \cong 3.5 \pm 0.1$. The good agreement of the experimental values of T_{in}/E_a (Table 6) with the theoretical result is an additional proof of the validity of this model and the mechanisms of oxalate decomposition.

Table 6

Average initial temperature/average activation energy ratio for the steady-state decomposition of oxalates in vacuum

Oxalate	\bar{T}_{in} (K)	\bar{E}_a (kJ mol ⁻¹)	$\bar{T}_{\text{in}}/\bar{E}_a$ (K mol kJ ⁻¹)	T_{in}/E_a^a (K mol kJ ⁻¹)
NiC_2O_4	536	157	3.4	3.5
MnC_2O_4	609	164	3.7	3.4
$\text{Ag}_2\text{C}_2\text{O}_4$	389	106	3.7	3.6
HgC_2O_4	413	109	3.8	3.5
PbC_2O_4	552	151	3.6	3.4

^a Ratio of the calculated values taken from Table 4.

3.3. Retardation of decomposition in the presence of gaseous products

An additional criterion for correct selection of the primary-product composition could come from a study of the depressing effect exerted on the decomposition rate by one of the assumed products introduced into the reactor in an excess amount. This results in a change not only of the decomposition mode and, hence, of the activation energy (see Section 2.2), but of the rate and temperature of decomposition as well. Therefore, a significant change in one of these parameters in the presence of a potential reaction product is a reliable indication of its correct identification. We used this criterion earlier in identifying the products of decomposition of ZnO and CdS [18] and then, of HgO [16].

Unfortunately, there are only a few studies where decomposition of oxalates was investigated in the presence (or in an atmosphere) of one of the potential products: CO, CO₂ or O₂. In Table 7, we summarise some of these results for Ag₂C₂O₄ and HgC₂O₄. Theoretical values of the retardation factor correspond to the ratios of the total equivalent pressures P_{Σ} in equimolar and isobaric modes of decomposition calculated with Eqs. (3) and (7), respectively. Experimental values of the retardation factor for Ag₂C₂O₄ correspond to the ratio of its decomposition rate in inert (N₂) atmosphere to that in air [30] or to that in oxygen [50] or, finally, to that in CO₂ [50]. The experimental value of the retardation factor for HgC₂O₄ corresponds to the ratio of its decomposition rate in vacuum to that in the presence of Hg vapour [32]. As can be seen from Table 7, calculations are in very satisfactory agreement with experiment. This factor is very sensitive to the composition of gaseous products. For the decomposition of Ag₂C₂O₄ into

2Ag(g) + 2CO₂, the retardation factor at 457 K in an atmosphere of CO₂ would be equal to 10⁴ instead of 15 (as listed in Table 7). For the decomposition of HgC₂O₄ into Hg(g) + 2CO₂, the retardation factor would be equal to 130 instead of 30.

Jacobs and Kureishy [34] have investigated the dependence of the decomposition rate of NiC₂O₄ on the CO₂ pressure in the reactor. Increasing the pressure from 54 to 384 Torr decreased the rate constant by a factor of 1.9. This is in very good agreement with the theoretically expected value: $(384/54)^{1/2.5} = 2.2$. For the decomposition of NiC₂O₄ into Ni(g) + 2CO₂, the retardation factor would be equal to 50. Therefore, all these experiments strongly support the suggested schemes of decomposition of Ag, Ni and Hg oxalates. The evolution of oxygen as free atoms during the HgC₂O₄ decomposition is in agreement with the decomposition scheme: HgO(s) → Hg(g) + O suggested and proved in [16]. Taking into account the implied schemes of decomposition of MnC₂O₄ and PbC₂O₄ (see Table 4), we can expect that the decomposition of both oxalates should be independent of the presence of CO₂ in the reactor.

3.4. Decomposition coefficients

By the coefficient of decomposition, α (or evaporation in the case of the sublimation of simple substances), one usually refers to the ratio of the real gaseous-product flux, J , to the flux, J_{\max} , from the effusion cell wherein the decomposition products are expected to attain their equilibrium partial pressures. Judging from numerous experimental measurements [22], $\alpha \ll 1$ for many substances, i.e. they decompose more slowly than expected based on effusion-cell experiments. This discrepancy is usually attributed to the multi-stage character of the evaporation process,

Table 7
Retardation of decomposition in the presence of gaseous product (X)

Oxalate	T (K)	P_x (atm)	P_{Σ} (atm)		Retardation factor		Refs.
			Equimolar	Isobaric	Calculated	Experimental	
Ag ₂ C ₂ O ₄	404	0.21 (O ₂)	2.2×10^{-5}	4.7×10^{-6}	5	4	[30]
	457	1.0 (O ₂)	7.3×10^{-4}	2.0×10^{-4}	4	2	[50]
	457	1.0 (CO ₂)	7.3×10^{-4}	4.7×10^{-5}	15	9	[50]
HgC ₂ O ₄	463	0.017 (Hg)	6.4×10^{-6}	2.1×10^{-7}	30	25	[32]

Table 8

Total equilibrium pressures of gaseous species and coefficients of decomposition for the oxalates under study at the initial decomposition temperatures

Equilibrium	Initial decomposition temperature (K)	Equilibrium pressure (atm)	Coefficient of decomposition
$\text{NiC}_2\text{O}_4 = \text{Ni (s)} + 2\text{CO}_2$	568	2×10^5	5×10^{-12}
$\text{MnC}_2\text{O}_4 = \text{MnO (s)} + \text{CO} + \text{CO}_2$	651	4×10^3	2.5×10^{-10}
$\text{Ag}_2\text{C}_2\text{O}_4 = 2\text{Ag (s)} + 2\text{CO}_2$	363	1×10^{17}	1×10^{-23}
$\text{HgC}_2\text{O}_4 = \text{Hg (l)} + 2\text{CO}_2$	424	5×10^{16}	2×10^{-23}
$\text{PbC}_2\text{O}_4 = \text{PbO (s)} + \text{CO} + \text{CO}_2$	532	5×10^2	2×10^{-9}

specific features of surface relief and impurities and lattice defects of the reactant [22]. L'vov and Novichikhin [18] attempted to explain this as due to the difference between the true scheme of thermal decomposition of a given compound and one which assumes direct decomposition to the final products in thermodynamic equilibrium (as is the case in the effusion cell). These differences consist first, in primary gasification of all decomposition products, including low-volatility components (metals and metal oxides) and second, in a partial or total evolution of gaseous species in the form different from the equilibrium composition.

By properly choosing the primary-product composition we have succeeded in interpreting the low values of α for some azides [11], Ag_2O [15], HgO [16], AgNO_3 , BaSO_4 , BaCO_3 , Be_3N_2 , Mg_3N_2 , AlN , GaN , ZnO , CdS and CdSe [18]. In the same way, we have succeeded in explaining the low sublimation coefficients for P (red), As and Sb [18].

In Table 8, we present the results of estimation of the decomposition coefficients for the oxalates under study. It can be seen that the equilibrium pressure of gaseous products at the initial decomposition temperature is extremely high, especially for $\text{Ag}_2\text{C}_2\text{O}_4$ and HgC_2O_4 (both oxalates are explosives). As a result, the decomposition coefficients for all oxalates are very low. In this respect, they can be compared only with the decomposition coefficients for azides.

4. Conclusions

The main decomposition characteristics (the activation energies and initial decomposition temperatures) were used for the selection of appropriate schemes of thermal decomposition of nickel, manga-

nese, silver, mercury and lead oxalates. Two different schemes were selected: with the evolution of $\text{CO} + \text{CO}_2 + \frac{1}{2}\text{O}_2$ (or O) as primary products for Ag, Ni and Hg oxalates, and the evolution of $2\text{CO} + \frac{1}{2}\text{O}_2$, for Mn and Pb oxalates. The validity of the proposed decomposition schemes is supported by the good agreement of experimental values of E_a and T_{in} with their theoretical values calculated from the model of dissociative evaporation of the reactant with simultaneous condensation of the low-volatility product. As an additional criterion for correct selection of the primary-product composition, the depressing effect exerted on the decomposition rate by one of the assumed gaseous products was used. Some of the features of the oxalate decomposition were interpreted. Among them are the following: a tremendous difference between the high equilibrium partial pressure of gaseous species at the initial temperature of decomposition, on one hand, and the low equivalent partial pressure corresponding to the decomposition rate at this temperature, on the other; a striking correlation between T_{in} and E_a parameters; a difference between the activation energies for the induction and the acceleratory periods in the decomposition of NiC_2O_4 and $\text{Ag}_2\text{C}_2\text{O}_4$, and the existence of long induction periods for decompositions of all the oxalates except for HgC_2O_4 . Particular emphasis is placed on the difference between the equilibrium composition and the suggested composition of primary gaseous products. Some experimental approaches (based on quadruple MS or the study of retardation effects) are proposed to verify the suggested reaction schemes.

We are aware that interpretation of the composition of primary products for the decomposition reaction does not explain the origin of the decomposition process on the molecular level. It is quite possible that some of the well-known mechanisms associated

with the transport of electrons, protons, positive holes, or ions among groups of atoms or ions, are responsible for this or that particular disintegration scheme. However, we suppose that the explanation of these disintegration features is concealed in the crystalline structure of the reactant and the chemical bonds between its constituents. This was discussed in more details in [11,17].

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